

## ON THE CONNECTION BETWEEN SURFACE ORDERING TRANSITIONS AND HYDRATION FORCES BETWEEN TWO APPosed SURFACES

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We have generalized the hydration force theory by including a surface contribution to the total free energy that depends on the normal component of the order parameter at the surface. Furthermore we have investigated the characteristics of the repulsive pressure as a function of intersurface separation in the case where surface free energy exhibits multiple minima, corresponding to different surface ordering states, and allows transitions between them. We have shown that surface ordering transitions are mirrored as breaks in the hydration force curve.

### 1. Introduction

Hydration force theory, as set forth by Marčelja and Radić in their seminal work [1], brings together two concepts: the existence of a surface order described by a constant (surface) value of the normal component of a vectorial order parameter and the form of bulk correlations between water molecules exemplified by the exponentially decaying correlation function. The repulsive forces emerge as a consequence of the modification of the entropy of water in between the two surfaces, brought about by the propagation of surface order from two apposed surfaces into the bulk.

There have been several variations on this basic theme, most notably the nonlocal electrostatic treatment of the correlations [2] or the modifications in the forces brought about by imposing different boundary conditions at the surfaces [3]. The conclusions obtained from these basically phenomenological theories are not in contradiction with more detailed microscopic model calculations [4]. Alternative views on the hydration force theory have also been presented [5].

In this contribution our interests are centered on

the interrelation between the surface structure, described by a surface free energy density, and behavior of intersurface forces. The total free energy of the interacting system will be, in general, composed of the bulk energy, that is a regular function of the order parameter and its derivatives, while the surface energy will be assumed to display distinct minima (different surface ordering states) in the phase space defined by the normal surface component of the order parameter. We will show that the equilibrium state of such a system also imposes a definite form of the boundary condition on the order parameter, that can be derived from the total free energy variation. The main result of this work, based on the mean-field analysis, is the demonstration that a phase transition in the surface structure is mirrored in the intersurface separation dependence of the forces between the surfaces. Our analysis only applies to systems where the overall packing symmetry is not affected by the surface ordering transition, i.e. the geometric arrangement of the interacting surfaces (e.g. hexagonal lattice in the case of interacting DNA helices [7]) remains the same before and after the surface ordering transition. Moreover we will show that measurement of intersurface forces can provide valuable information on the free energy characteristics of an isolated surface.

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## 2. Analysis

Let us concentrate on the hydration forces between two surfaces located at  $z = \pm h$  and extending in the  $x, y$  directions. Our basic ansatz will be the free energy of the system as a function of a vectorial order parameter  $\mathbf{P}$ , that we can write in the general form

$$F = \int \left[ \frac{1}{2} \alpha (\operatorname{div} \mathbf{P})^2 + \frac{1}{2} \beta P^2 \right] dV + \oint \sigma(P_n) dS. \quad (1)$$

The first (volume) part of the above free energy is nothing but the standard form used in the Marčelja–Radić-type theories of the hydration force. The second term is new here. It corresponds to the energy contribution of the isolated surfaces and includes all the short range forces or packing constraints (it does not include the hydration self-energy) operating close by or at the surfaces. Due to symmetry considerations it can depend only on the normal component of the vectorial order parameter at the surfaces ( $P_n$ ).

The equilibrium profile of the order parameter can be obtained by setting the first variation of the above free energy functional equal to zero. Variational equations (Euler–Lagrange equations) decouple into two terms of which the first one is valid for variations of the order parameter in the bulk and has the standard form

$$\nabla^2 \mathbf{P} + (1/\xi^2) \mathbf{P} = 0, \quad (2)$$

where  $\xi^2 = \alpha/\beta$ . The second equation, stemming from the variation of the normal component of the order parameter at the two surfaces, leads to the following condition:

$$\alpha (\operatorname{div} \mathbf{P}) + \partial \sigma(P_n) / \partial P_n = 0. \quad (3)$$

Basically the variational equation for the free energy therefore determines the equilibrium profile of  $\mathbf{P}$  as well as the self-consistent boundary condition at the two surfaces. In the parallel plane case the solution of eq. (2) reads

$$\mathbf{P} = (P_x, P_y, P_z) = (0, 0, P_n \sinh(z/\xi) / \sinh(h/\xi)).$$

The boundary condition eq. (3) therefore takes the form

$$(\alpha/\xi) P_n \coth(h/\xi) + \partial \sigma(P_n) / \partial P_n = 0. \quad (4)$$

Solution of the above equation gives the surface

value of  $P_n$  as a function of  $h$ . The Marčelja–Radić boundary condition, i.e.  $P_n = P_0$  [1], is now recovered from eq. (4) if  $\sigma(P_n)$  has a very steep minimum at  $P_0$ , therefore if  $\sigma(P_n) = \gamma(P_n - P_0)^2$  with  $\gamma \gg 1$ . On the other hand the boundary condition used by Cevc et al. [3] is regained if  $\sigma(P_n) = F P_n$ , where  $F$  can be interpreted as a constant surface orienting field. Clearly in the limit of infinite separation eq. (4) states that the equilibrium value of  $P_n$  is given by minimizing the total surface energy  $\sigma'(P_n)$  composed of  $\sigma(P_n)$  and hydration self-energy,

$$\sigma'(P_n) = \sigma(P_n) + (\alpha/2\xi) P_n^2. \quad (5)$$

If  $\sigma(P_n)$  is known, the repulsive pressure can be obtained straightforwardly by solving the self-consistent boundary condition eq. (4) as

$$p(h) = -\frac{1}{2} (\partial/\partial h) (F/S) \\ = -\frac{1}{4} (\alpha/\xi^2) P_n^2(h) \sinh^{-2}(h/\xi). \quad (6)$$

Evidently the dependence of repulsive pressure on intersurface separation  $2h$  comes from two sources. First of all there is the direct interaction between the two surfaces embodied in the  $\sinh^{-2}(h/\xi)$  factor that depends only on the form of the bulk correlation function. The indirect interaction comes from dependence of  $P_n$  on  $h$  and is determined by the form of  $\sigma(P_n)$  through the self-consistent boundary condition. In the limit of large spacings we remain with  $p(h \rightarrow \infty) \approx -[\alpha P_n^2(\infty)/\xi^2] \exp(-2h/\xi)$ , where  $P_n(\infty)$  is determined from the minimum of  $\sigma'(P_n)$ .

In what follows we shall consider some nontrivial models for the surface structure embodied in  $\sigma(P_n)$ . The basic assumption will be that there exist different surface ordering states, described by different values of  $P_n$ , that show up as multiple minima in the  $\sigma(P_n)$  function. We will show that repulsive forces operating between the two surfaces can drive transitions between these different surface ordering states that in turn modify the characteristics of the forces themselves. In general, surface ordering transition will show as a break in the  $p(h)$  curve.

## 3. The second-order transition

Since it presents an analytically tractable case we shall start with the surface free energy density of the

form

$$\sigma(P_n) = -\frac{1}{2}aP_n^2 + \frac{1}{4}bP_n^4,$$

with  $a, b > 0$ . The equilibrium state of an isolated surface is now obtained from eq. (4) with  $h \rightarrow \infty$ , leading to a single stable state, viz.  $P_n = [(a - \alpha/\xi)/b]^{1/2}$ , if we suppose that  $a - \alpha/\xi \geq 0$ . As the second surface approaches the equilibrium configuration is modified, depending on the value of  $h$ . The stable solutions of eq. (4) are now given as

$$P_n = 0, \quad a - (\alpha/\xi) \coth(h/\xi) < 0, \quad (7)$$

$$P_n = \left( \frac{a - (\alpha/\xi) \coth(h/\xi)}{b} \right)^{1/2}, \quad a - (\alpha/\xi) \coth(h/\xi) \geq 0. \quad (8)$$

Clearly the situation for a finite  $h$  is more complex than in the case of a single, isolated surface. There exists a finite value of  $h = h_c$ , given by the solution of  $a - (\alpha/\xi) \coth(h_c/\xi) = 0$ , where there is a continuous (second-order) transition from a state with nonzero  $P_n$  to a state with  $P_n = 0$ . If  $a - \alpha/\xi < 0$ , then  $P_n = 0$  is the stable configuration at all values of  $h$ .

The corresponding free energy obtained from eq. (1) can be written as

$$F/S = -\frac{1}{2} \frac{[a - (\alpha/\xi) \coth(h/\xi)]^2}{b},$$

if  $a - (\alpha/\xi) \coth(h/\xi) \geq 0$ . Otherwise it is zero. The transition from the state with  $P_n \neq 0$  to the state with  $P_n = 0$  is therefore accompanied with a break in the curve describing the dependence of the free energy on the separation, see fig. 1. The same situation is seen for pressure as a function of  $h$  that can be obtained as

$$p = -\frac{1}{2}(\alpha/\xi b) [a - (\alpha/\xi) \coth(h/\xi)] \sinh^{-2}(h/\xi)$$

if  $a - (\alpha/\xi) \coth(h/\xi) \geq 0$  and zero otherwise. The second-order phase transition in  $P_n$ , triggered by interactions between the two surfaces, is therefore transformed into a break in the curve describing the interaction free energy as a function of  $h$ . The intersurface forces therefore drive the surfaces from one stable state into another one, the transition itself being accompanied by a brake in the functional de-

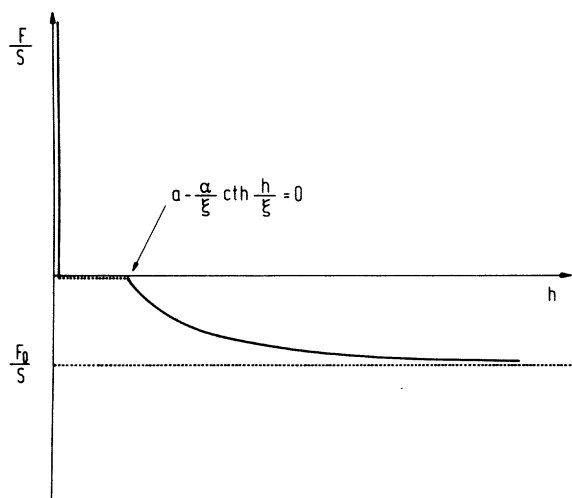


Fig. 1. Dependence of the free energy on  $h$  in the case of a second-order surface ordering transition. The break in the curve is obtained for  $h = h_c$ , where  $h_c$  is the solution of  $a - (\alpha/\xi) \coth(h_c/\xi) = 0$ . At large enough values of  $h$  the dependence of  $F(h)$  is approximately exponential. The value of  $F_0/S = -[a - (\alpha/\xi)]^2/2b$ . At small separations ( $h \rightarrow 0$ ) the steric repulsion leads to large positive  $F$ .

pendence of the interaction free energy (or equivalently pressure) on  $h$ .

#### 4. The first-order transition

We shall next treat the case where the total surface free energy density  $\sigma(P_n)$ , that includes the hydration self-energy as in eq. (5), has two distinct minima,  $P_0$  and  $P_1$ , both at nonzero values of  $P_n$ , see fig. 2. An analytical solution of eq. (4) in this case is not readily available and we shall make use of the graphical construction similar to the one used by Cahn in his analysis of the wetting transition [6]. First of all we note that we can rewrite the surface part of the Euler-Lagrange equation eq. (3) as

$$(\alpha/\xi)P_n(h) [\coth(h/\xi) - 1] + \partial\sigma'(P_n)/\partial P_n = 0. \quad (9)$$

The graphical solution of this equation,  $P_n(h)$ , is obtained from the intersection of two curves in fig. 3. At large values of  $h$  the solution of eq. (9) is located close to  $P_1$  since this state corresponds to the global minimum of the free energy. Pushing the two surfaces together  $P_n(h)$  moves continuously towards

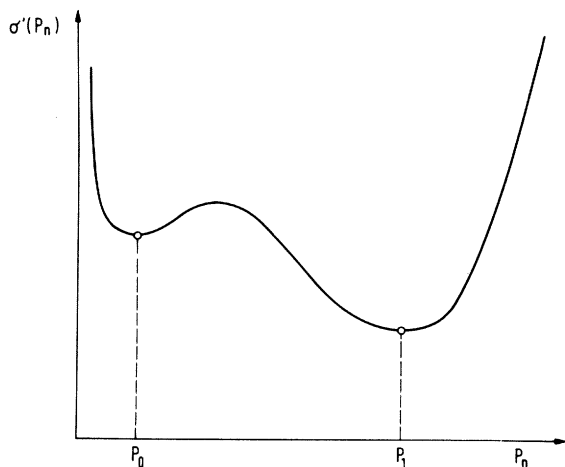


Fig. 2. A hypothetical form of  $\sigma'(P_n) = \sigma(P_n) + (\alpha/2\xi)P_n^2$  that exhibits two minima at different values of  $P_n$ . The minimum at  $P_1$  is supposed to be deeper and it would correspond to a stable configuration of an isolated surface, i.e.  $P_n(h \rightarrow \infty) = P_1$ .

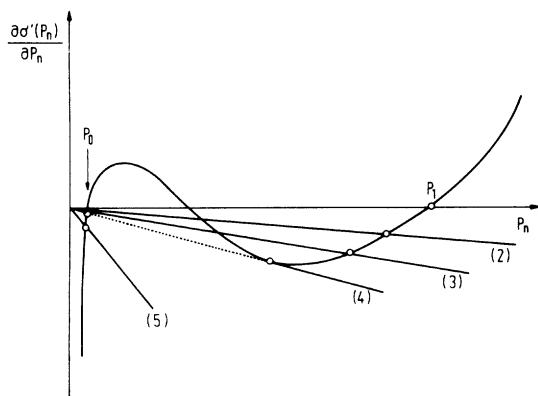


Fig. 3. The solution of eq. (9) is given as the intersection of the straight lines with  $\partial\sigma'(P_n)/\partial P_n$ , where the hypothetical form of  $\sigma'(P_n)$  is shown in fig. 2. The straight lines correspond to linear terms (in  $P_n$ ) in eq. (9) with the coefficient proportional to  $\coth(h/\xi) - 1$ . Each line, labelled (2, 3, 4, 5), corresponds to a different value of  $h$ ,  $h_{i+1} < h_i$ . At a critical value of  $h = h_c$  there is a jump from one branch of the  $\sigma'(P_n)$  curve, close to the surface ordering state described by  $P_1$ , to the other one close to  $P_0$ . The stable solutions of eq. (9) are shown as open circles.

smaller values until at a critical value of  $h = h_c$  it jumps from one stable branch of the  $\sigma'(P_n)$  curve to another one. The value of  $h_c$  is given as a solution of eq. (9) and

$$-(\alpha/\xi) [\coth(h_c/\xi) - 1] = \partial^2 \sigma'(P_n) / \partial P_n^2.$$

If we now plot the corresponding pressure  $p$  as a function of  $h$ , we get an "isotherm" in the  $(p, h)$  diagram, fig. 4, where the discontinuity at  $h_c$  corresponds to the jump in  $P_n$  at  $h_c$ . The two branches of the  $p(h)$  curve evidently correspond to different surface "phases" (ordering states) as displayed by the existence of two distinct minima in the  $\sigma'(P_n)$  curve. Since the system is supposed to be in equilibrium there is another condition that we have to take into account, i.e. the equality of chemical potentials in the two "phase" region of the transition from one branch of the  $p(h)$  curve to the other one. This leads to the condition

$$\int_{h^-}^{h^+} h dp = 0, \quad (10)$$

which is the Maxwell equal area rule, see fig. 4. The transition from one branch of the  $p(h)$  curve to the other one can therefore only be accomplished at a value of  $p = p_t$  given by eq. (10). At  $p_t$  the surfaces would jump from  $h^+$  on one branch of the  $p(h)$  curve to  $h^-$  on the other one (see fig. 4). We can easily derive the connection between the values of  $P_n$  at this transition point and  $\Delta h = h^+ - h^-$ , viz.

$$[P_n(h^-)/P_n(h^+)]^2 \exp(2\Delta h/\xi) \approx 1.$$

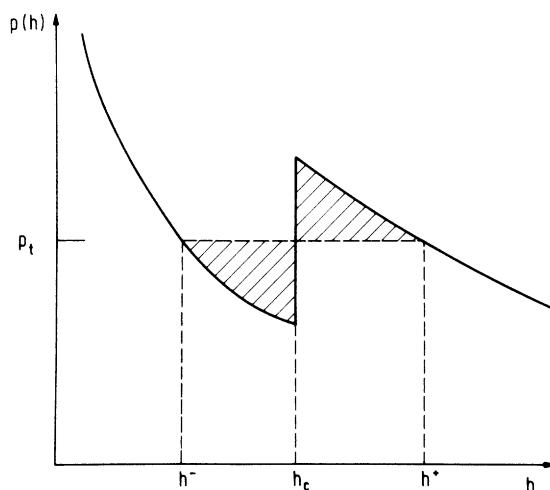


Fig. 4. Dependence of the repulsive pressure, eq. (6), on  $h$ . The two branches of the  $p(h)$  curve correspond to two stable branches of the solution  $P_n(h)$  obtained graphically on fig. (3). The transition between the two branches is governed by the Maxwell construction that demands the equality of the two hatched areas.

There is another general characteristics of the  $p(h)$  curve that we want to discuss. If we try to approximate  $p(h)$  by an exponential function with an effective decay length  $\zeta$ , its value for  $h \geq h^+$  is different from its value after the transition at  $h \leq h^-$ . This can be seen by inspecting fig. 3. For  $h > h^+$   $P_n(h)$  is an increasing function of  $h$ , meaning that the repulsive pressure eq. (6) would fall off more slowly with separation than indicated by the  $\sinh^{-2}(h/\xi)$  (or equivalently  $\exp(-2h/\xi)$  at large enough  $h$ ) factor. Therefore in this regime  $\zeta > \xi$ . If on the other hand, as we supposed when drawing fig. 3,  $\sigma'(P_n)$  is steeper for  $P_n < P_0$  than it is for  $P_n(h^+) < P_n < P_1$ , then  $P_n(h < h^-)$  would be approximately constant, meaning that in this regime  $\zeta \approx \xi$ . The assumption of differing steepnesses of the  $\sigma'(P_n)$  function is certainly plausible for highly polar surfaces that would vigorously oppose all the states of vanishing or even reversed water orientation (proportional to the normal component of the order parameter).

## 5. Discussion

In this contribution we have generalized the phenomenological theory of the hydration force by including the surface contribution to the total free energy that leads to a self-consistent form of the boundary condition. We have used this modification to analyse the consequences of surface ordering transitions on the characteristics of the forces acting between the surfaces. We were able to show that the first- and second-order surface transitions will show as breaks in the force curves. Furthermore, in the case of a first-order transition, the effective decay lengths of the repulsive pressure before and after the transition are in general different, depending on the steepness of the function  $\sigma(P_n)$  close to the two minima.

Recent measurements of forces between PEG collapsed DNA helices [7] with hexagonal packing geometry in the presence of small concentrations of different ligands such as polyamines, protamine, cobalt hexamine, Mn and Cd all show clear breaks in the force curves and different decay lengths before and after the breaks, all in qualitative agreement with the statements made above for systems that exhibit surface ordering transitions. Since these ions appear

to sit inside the grooves of the double helix rather than in between the interacting molecules it is natural to assume that they will mostly affect the local water ordering at the macromolecular surfaces. Our formalism would be perfectly suited for description of such situations. An independent measurement of the local order (with e.g.  $^2\text{H-NMR}$  of  $^2\text{H}_2\text{O}$ ) at the macromolecular surfaces just before and after the break in the force curve would provide an additional criterion whether the situation can really be understood in the framework of surface ordering transitions. Furthermore at large enough concentrations of ligands one can observe spontaneous collapse of DNA without any additional PEG stress. This situation is more complex than in the case of small concentrations since it leads to a symmetry change during the collapse transition and cannot be understood in terms of a simple surface ordering transition alone. Additional features have to be brought into consideration for those cases [7].

At the end let us add that due to the experimental means available for the study of interacting surfaces the primary role is played by the measured repulsive pressure and not by the form of  $\sigma(P_n)$ . However, based on our analysis, there exists a neat way to extract the behavior of  $\sigma'(P_n)$  from the measured forces. Starting from eq. (4) we are led to the following connection between  $\sigma'(P_n)$  and  $p(h)$

$$\begin{aligned} \sigma'(P_n) - \sigma'(P_1) \\ = -2 \int_{\infty}^h p(h) dh - \xi p(h) [1 - \exp(-2h/\xi)] . \end{aligned}$$

The measurement of forces could therefore provide us also with direct information on the surface free energy density of an isolated surface as a function of  $P_n$ . No hypothetical form of  $\sigma(P_n)$  would have to be assumed but could be derived directly from experiment. We shall follow this line of reasoning in a separate publication.

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